Chapter 2
Review of Media Filtration for Stormwater Quality Control

Sand

The use of sand filtration is common for drinking water and sanitary wastewater treatment/effluent polishing. Water supply treatment plants have successfully used sand filtration for many years. Wastewater treatment plants often use sand filtration to polish their effluent before release, especially as the regulatory requirements for the discharge of suspended solids becomes more stringent. Sand filters are also popular as stormwater runoff treatment, especially in urban areas where the filters must be retrofitted and property values decree that the filters be located underground (Claytor and Schueler 1996).

Physical Characteristics

Slow sand filters are characterized by slow filtration rates, an extremely narrow range of sand particle sizes, the lack of chemical pretreatment, relatively long filter runs between cleanings, and surface scraping and sand removal instead of backwashing as a cleaning technique (Collins*, et al.* 1992). Filtration rates are as much as fifty times slower than those of rapid sand filters; consequently, slow sand filters require significantly more surface area in order to filter comparable volumes of water (Crittenden*, et al.* 1993). Slow sand filter media is characterized by certain parameters: size distribution, settling velocity, porosity, grain integrity, shape, hardness (resistance to attrition), and the results of visual and microscopic examinations (Ives 1990). Slow sand filters need to have a minimum vertical distance (or fall) of at least 0.6 m, but preferably 1.5 m, from inflow to outflow to drive the water by gravity through the entire filter (Claytor and Schueler 1996).

Fine sand/silt filters remove particulates by direct straining on the surface of the filter media. The combination of grain size and bed depth will determine the effectiveness of the filter. Naghavi and Malone (1986) demonstrated that the combination of grain size (0.2 mm) and a shallow bed depth produced an average fluorescence removal of approximately 97%, even with no chemical pretreatment. This combination also had the highest initial filtration rate (226 m^3 m^{-2} day^{-1}) and a lower initial headloss (7.3 cm). The effect of media size on filtering ability also was demonstrated by Tobiason*, et al.* (1993) in a 2.5 cm inner diameter (ID) acrylic column filled with 17 cm of 0.4 mm glass beads along with the test suspensions that contained either one size or a mixture of 0.27, 1.3 and 10 μm diameter particles. The use of smaller diameter media affected the rate of removal of larger particles and the rate of head-loss development. Head-loss development was typically linear with time, and, for suspensions of mixed particle sizes, it generally was the same as, or somewhat lower than, head loss for monodisperse suspensions of the smaller-sized particle (Tobiason*, et al.* 1993). Head loss (or hydraulic resistance) is determined by the filter's surface area, which depends on the size and number of grains, not the grains' weight. In order to have the same head loss development pattern in a 'single-size' media filter, the new filter would require a diameter equal to the d_{10} of the mixed-size media (Ives 1990). Head loss results from increased fluid drag, pore constriction, and increased interstitial velocities caused by particle deposition. Small particles cause more head loss because of their high surface area per unit volume (Tobiason*, et al.* 1993). Head loss is spread more evenly through the filter in larger particle diameter media. Therefore, capturing a particle with larger diameter media results in less head loss than capturing it with smaller media (Clark*, et al.* 1992).

Removal is different at the various depths of the filter, with the influent particle concentration being reduced dramatically in the top section of the filter and smaller reductions occurring near the bottom of

the filter. This effect is most pronounced for filters with smaller sand sizes; therefore, removal efficiency in the larger media improves substantially compared to the smaller media at each successive depth of the filter. Later in the filter run, large particles apparently are less effectively removed in the top section of the filter, suggesting that small particles entered the filter and were captured by previously retained particles, thereby forming a floc on the media surface. If the flocs break off the surface, they may pass unhindered through the filter media and be measured as larger particles. In addition, particles with surface chemistry favorable for retention in the medium likely are captured in the top section of the filter while the particles with unfavorable surface chemistry reach the lower section where they still are not removed from solution (Clark*, et al.* 1992). Percent removal is a function of both sand depth and particle size; using coarse sand and a deep bed is recommended by Farooq and Al-Yousef (1993) because this type bed will require less cleaning than fine sand in a shallow bed filter.

Filtration velocity, to a lesser extent than media size, affects removal efficiency, bed depth use, and head loss. Head loss is directly proportional to velocity in new filters, but for ripened filter beds, the direct proportionality does not apply. Increased velocity pushes particles deeper into the filter bed prior to capture, thus allowing more of the filter depth to be used in particle capture. This leads to reduced head loss and, therefore, larger quantities of water can be treated before cleaning (Clark*, et al.* 1992). There is, however, an upper limit on filtration velocity. At loading rates higher than 5 m/day of sanitary wastewater, the sand filter clogs within a few days while for loadings less than 1 m/day, collected organic particles decompose in the filter and free up pore space, and the run length on a volume-treated basis is quadrupled (Fujii*, et al.* 1987).

For sand, as for other filter media, the shape of the curve of percent captured versus particle diameter depends on the particle capture mechanism, the filter medium, the fluid being filtered, and the filtration conditions (Shucosky 1987). Generally, dissolved oxygen concentrations and pH decrease in sand filtration. Particulate chemical oxygen demand (COD), particulate organic nitrogen, and particulate phosphorus are removed during filtration, even before the filter is ripened. However, very little of the soluble fraction of the above constituents is removed (Fujii*, et al.* 1987).

Using lateral viewing endoscopes, unexpected phenomena, such as tumbling grain motion and void formation ('wormholes,' or pores larger than a sand particle's diameter), have been observed in traditional sand filters, especially rapid filters or those using countercurrent filtration. These 'wormholes' start with holes in the surface deposit and remain open despite the continuing flow of solids into them. Aggregates, especially those of weakly-bound compounds, that enter the wormholes, even if they are larger than the hole, may be deformed or disrupted by the hole, yet they do not completely stop flow through the hole. This aggregate 'destruction' during filtration only occurs to an appreciable extent when substantial surface deposits are present (Ives 1989). Preferential flow (macropore, fingering, or funneled flow) also has been observed in sand filters, as it has in many other filters and soils. During preferential flow, the fluid follows the local wetting front in wormholes and bypasses the matrix pore space. Filtration efficiency for preferential flow pathways is much smaller than it is for matrix pore flow because flow through preferential pathways is more rapid and less time is available for straining and/or sorption (Steenhuis*, et al.* 1980).

General Removal Capabilities
Slow sand filters are extremely effective in removing suspended particles, and effluent turbidities are consistently below 1.0 NTU. Bacteria, viruses and *Giardia* cysts are also removed with enhanced filtration once a bacterial population is established on the filter. However, sand filters have only a limited ability to remove organic material that are precursors to trihalomethane formation and the biodegradable fraction of dissolved organic carbon (BDOC) (Collins*, et al.* 1992; Eighmy*, et al.* 1992; Farooq and Al-Yousef 1993). Stratified sand filters have been shown to remove enteric viruses, along with total organic carbon (TOC) from septic tank effluent at a loading rate of 0.061m/day, even from sand filters that contained new sand, i.e., had no bacterial biofilm ("schmutzdecke") and, therefore, no bacterial breakdown of pollutants (Gross and Mitchell 1990). A sand filter with an effective grain size of 0.23 mm and a loading rate of 3.84 m/day was shown to effectively remove biochemical oxygen demand (BOD) (86%), suspended solids (68%), turbidity (88%), and total coliform bacteria (99%) from sanitary wastewater (Farooq and Al-Yousef 1993).

High algae removal can be accomplished using media with median sand size ≤ 0.2 mm (Naghavi and Malone 1986). Sand filtration at a Superfund site showed suspended solids removal of about 50% for waters that contained mostly colloidal-sized particles and 80% to 100% removal for waters whose solids were larger. One unexpected result for the filtration was that solids breakthrough occurred much earlier than expected, possibly because the filter was not in continuous operation (Dahab, *et al.* 1991). The presence of wormholes was not investigated by Dahab, *et al.* (1991) although this is one potential explanation for the early breakthrough.

Sand filtration, without modification of the sand by ripening or by adding a surface coating of an adsorber such as manganese or ferric oxide, is not effective at removing dissolved constituents. Deethylatrazine was consistently detected in the effluent of one sand filter (2 cm ID x 30 cm long filter) used to treat natural groundwater spiked with 200 μg/L of atrazine (applied at 5 mL/min for 70 days; 23 m^3 m^{-2} day^{-1}) until the filter ripened, when it was no longer detected (Selim and Wang 1994). Sand filtration also does not remove total suspended solids (TSS) from pulp and paper mill secondary effluent as effectively as it does from municipal secondary effluent, likely because the nature and size of the solids are considerably different (unimodal at 2 μm) from the nature and size of the organisms filtered from secondary wastewater (bimodal at 4 and 85 μm). The pulp and paper mill effluent had mostly very small particles, a range where the sand filter is not as effective (Biskner, *et al.* 1978).

Ripening of the Sand Filter

Ripening is the development of a bacterial biofilm, the 'schmutzdecke,' on the sand filter that improves the removal ability of the filter. This increased efficiency occurs for all particle sizes initially, but eventually only continues for small sizes with the removal efficiency decreasing and possibly becoming negative for larger particles. Captured particles aid in the collection of subsequent particles by partially blocking and restricting passage through the pores. Therefore, the rate of increase in particle removal efficiency depends on the influent particle concentration. When more time elapses between collisions of particles on the media surface and those in solution, the first collected particle may migrate to the bottom of the grain and greatly reduce the opportunity for interaction with the next incoming particle. Thus, the removal efficiency is greater and ripening is quicker when the influent concentration is greater (Clark, *et al.* 1992).

Submicron particles also improve the deposition of larger particles because they increase the apparent surface roughness of the media and/or the large particle (Tobiason, *et al.* 1993). Ripening of the filter creates rougher pore channels, which slows down the flow and provides more contact time between the media and the pollutants in the water (Fujii, *et al.* 1987). In addition, larger particles may hinder the initial deposition of the smaller particles because of unfavorable hydrodynamic interactions or differences in destabilization (Tobiason, *et al.* 1993).

Sand filters have a more limited capacity for substrate growth and thus have a smaller microbial population, as compared to organic media filters of the same size (Selim and Wang 1994). Even when ripening is complete, head-loss development is approximately linear with time (or mass deposited) (Tobiason, *et al.* 1993).

Adsorbent Coatings

Another technique for improving the removal efficiency of a sand filter is by adding an adsorbent coating, usually an iron or manganese oxide, to the sand grains, thus providing adsorption sites for the ions in solution. Potential sorption mechanisms include diffusion into the lattice of the minerals; adsorbing at sites on the sand surface; adsorbing sites on hydrous iron and manganese oxides and hydroxides; and complexing at sites on natural organic matter in the schmutzdecke. The iron oxide coating on sandy soil has been found to bind metals of all sizes very strongly. Metal binding strength is relatively low in the exchangeable fraction (the portion of the pollutant concentration that participates in ion-exchange rather than in complexation or chemisorption) and increases in the non-exchangeable fraction because metals in the non-exchangeable fraction likely are incorporated within the crystalline lattice or strongly sorbed to the mineral surface. The non-exchangeable fraction, therefore, is 'permanently bound' to the sand under

normal operating conditions. The non-exchangeable fraction also contains the greatest concentration of sorbed metals, except zinc. The smallest sized media have the greatest mass concentration of metals. Lead binds more strongly to the smaller particles while arsenic, copper, and zinc show similar affinities for all size fractions. Metal sorption kinetics show the existence of both a fast reaction, where metals bind to surface sites, and a slow reaction, where metals bind to interior sites. Reaction kinetics also affect the availability of metals for sorption. Metals from the dissolution of the soluble compounds are available more quickly for sorption while metals in precipitates or other covalently bonded compounds are not (Van Benschoten, *et al.* 1994).

Manganese oxide coatings can remove manganese(II) from solution with the rate of sorption being positively correlated to the number of available surface adsorption sites. Chlorine in the manganese(II)-containing influent will oxidize the adsorbed manganese(II) and, therefore, continually regenerate the filter. Removal efficiency is a function of the surface MnO_x(s) concentration, its oxidation state, and the influent pH. Manganese(II) sorption capacity is greater, and the reaction rate is faster when the influent pH is raised (reducing H^+ ion competition for sites). For a given pH, sorption capacity also is increased as the surface MnO_x(s) concentration is increased. Efficient manganese(II) sorption was found even during the winter when the sorption rates likely are significantly slower. Further research has shown that the coatings do not affect the filter hydraulics either during a run or during cleaning, the clean-bed head loss of the filter, or the effective size and density of the filter media (Knocke, *et al.* 1991).

Limitations
Slow sand filtration has the following limitations and concerns: (1) a limited acceptable range of influents (usually less than two hundred milligrams per liter influent total suspended solids [TSS]); (2) a limited ability to remove organic precursor materials because of a lack of sorption surfaces; and (3) extensive filter downtimes and ripening periods (Collins, *et al.* 1992).

Cleaning and re-ripening a slow sand filter is difficult and time-consuming; however, several techniques have been developed to "speed up" that process. Wet harrowing in West Hartford, CT, removed the surface mat yet kept the biomass in the filter media down to the depth of harrowing (Eighmy, *et al.* 1992). Nonwoven, synthetic fabrics have been placed on the sand surface. The fabric has a greater porosity and specific area and is a more efficient filter for larger particles. The benefits of filter mats/fabrics placed on top of the sand surface are longer run times and simpler cleaning that requires only the removal and cleaning of the fabric. However, a filter cover does not improve the ability of a sand filter to treat raw waters of varying quality, and no suitable cleaning method exists for the fabrics in large-scale installations (Collins, *et al.* 1992).

Stormwater Runoff Treatment
Sand filtration for stormwater treatment began on a large scale in Austin, TX. The Austin sand filters are used both for single sites and for drainage areas less than fifty acres. The filters are designed to hold and treat the first one-half inch of runoff with very good pollutant removal ability.

According to the City of Austin design guidelines, the minimum sand depth should be eighteen inches. These filters may have either gravel, a geotextile, or other fabric on top of the sand to prevent premature clogging with large particles. For a filter built according to Austin's design guidelines, the assumed pollutant removal efficiencies, which are based upon the preliminary results of the City's stormwater monitoring program, are given in Table 13.

In Washington, D.C., sand filters are used both to improve water quality and to slow the runoff in order to prevent large slug inputs to the combined sewer system (CSO). Water quality filters are designed to retain and treat three-tenths to one-half inch of runoff with the exact design based upon the amount of impervious area in the watershed (Shaver 1994).

In Delaware, the sand filter is an acceptable method for achieving the 80% suspended solids reduction requirement. These filters are intended for sites that have impervious areas that will drain directly to the

filter, such as fast-food restaurants and gas stations. In many areas, sand filters precede an infiltration device in order to prevent or postpone clogging of the infiltration device. Sand filters are also used on sites where there is no space to retrofit other infiltration devices (Shaver 1994).

Table 13. Pollutant removal efficiencies for sand filters (Source: City of Austin 1988)

Pollutant	Removal Efficiency (%)
Fecal Coliform Bacteria	76
Total Suspended Solids (TSS)	70
Total Nitrogen	21
Total Kheldajl Nitrogen	46
Nitrate – Nitrogen	0
Total Phosphorus	33
Biochemical Oxygen Demand (BOD)	70
Total Organic Carbon	48
Iron	45
Lead	45
Zinc	45

According to Delaware's guidelines, the sand filter can be expected to adequately remove particulates (TSS removal efficiency 75 - 85 %) but not soluble compounds. Studies of a six-year old sand filter in Maryland that was installed at the drain of a heavily-used parking lot showed that the filter is now becoming clogged. Inspection of the sand below the filter surface has shown that oil, grease, and finer sediments have migrated into the filter, but only to a depth of approximately two to three inches (Shaver 1994; Galli 1990).

The sand filter used in Delaware has a similar design to the Austin filters with an eighteen-inch sand depth and a six-inch gravel underdrain. Each filter has a minimum of six to twelve inches of ponding depth/storage head available on top of the filter. Monitoring of a Delaware sand filter which treats the runoff from a 0.28 ha (0.7 acre) section of a parking lot near National Airport in Alexandria, VA, showed that the filter had an average 72% removal of total phosphorus, >80% removal of total suspended solids (influent concentration = 50 mg/L), and >90% removal of zinc (200-630 μg/L influent concentration). The sand filter, which had an underdrain layer, continued to function during freezing weather. Anaerobic conditions will develop in sand filters unless the bottom of the filter is exposed to air. Anaerobic conditions enhance nitrate removal by denitrification but reduce total phosphorus removal because the iron phosphates degrade and release phosphorus (Galli 1990).

Monitoring of a Delaware sand filter at the Alaska Marine Terminal in Seattle showed >80% removal of total petroleum hydrocarbons (TPH) when influent concentrations were 1.2 mg/L and >90% removal of TPH when influent concentrations were 3.1 mg/L. Suspended solids and phosphorus removals were similar to those noted at the National Airport in Alexandria, VA (Galli 1990).

Herrera Environmental Consultants (1991 and 1995) also have evaluated sand filters as a media for stormwater treatment. Their results indicate that sand filters by themselves are the least effective at removing both total phosphorus (0 to 28 percent removal) and soluble phosphorus (0 to 38 percent removal). Iron sand and sand amended with other constituents, such as calcitic lime and hypnum peat, were found to remove significantly more total phosphorus and soluble phosphorus than sand alone. The sand/calcitic lime mixture removed between 29 and 79 percent of the total phosphorus and between 25 and 93 percent of the soluble reactive phosphorus. The sand/hypnum peat mixture removed between 31 and 94 percent of the total phosphorus and 36 to 99 percent of the soluble reactive phosphorus (Herrera Environmental Consultants 1991). The addition of steel wool to the sand filter as an adsorbent showed that it was also an effective sorbent media for total and soluble phosphorus removal. Phosphorus removal occurs because the steel wool oxidizes in the presence of water and oxygen and the oxidized iron easily reacts with the phosphate in solution (Herrera Environmental Consultants 1995).

Urbonas (1999) has broken the stormwater detention and filtration process down into the individual unit processes that occur in a sand filter during suspended solids removal and has provided recommendations for using the information gathered during the unit process analysis to design new sand filter installations. Hydraulic capacity, a function of the suspended solids loading, is the design variable. This approach of Urbonas is novel in stormwater filter design because maintenance is addressed as a design variable in the sizing calculations, i.e., the recurrence interval of maintenance is used in the calculation of the amount of suspended solids removed per square foot of filter surface area.

Activated Carbon

Activated carbon separation has long been used in the water treatment and chemical process industries and in hazardous waste cleanup as an effective method for removing trace organics from a liquid. Activated carbon is made first by charring materials such as almond, coconut and walnut hulls, other woods or coal. The char particles are activated by exposing them to an oxidizing gas at high temperatures. The activation process makes the particles porous which creates a large internal surface area available for adsorption (Metcalf and Eddy 1991).

Organic Removal Capability

Activated carbon has been used for more than fifty years in drinking water treatment plants to remove taste- and odor-causing compounds, along with most synthetic organic chemicals, pesticides, herbicides, color, and trihalomethane precursors (Rael*, et al.* 1995). Disinfection by-products, including the trihalomethane precursors, have also been removed from drinking water by granular activated carbon (GAC) (Crittenden*, et al.* 1993; Abuzald and Nakhla 1994).

Slow GAC filters achieve excellent organic removals (> 90 percent), with the removal efficiency limited by the depth of the filter. This dependence is due to 'slowness' of the transport kinetics and attachment mechanisms inherent in activated carbon sorption. The problem with activated carbon is its exponential head loss curve, *i.e.*, increasing removal increases head loss development rates, and, therefore, the filters must be cleaned more frequently (Collins*, et al.* 1992).

Anaerobic charcoal chip reactors, along with anaerobic sand packed reactors, can remove up to 80% of the chemical oxygen demand (COD) at an organic loading rate of 7 kg COD/m^3-d and 60% at 12 kg COD/m^3-d and were able to withstand a shock loading of over 22 kg COD/m^3-d. However, efficiency dropped when wastewaters contained a high concentration of SO_4^{2-} and Na^+. In general, the removal efficiency of COD is inversely related to loading rates, and no clogging was observed even after one year of operation (Chin 1989).

Granular activated carbon (GAC) is useful for treating wastewaters with inhibitory, yet adsorbable, compounds that make conventional biological treatment difficult or impossible (Fox*, et al.* 1990). Activated carbon can remove both dissolved and synthetic organic carbon (DOC and SOC, respectively) compounds from solution. However, provided that adequate contact time exists in the treatment system, equilibrium capacity of the carbon decreases with decreasing initial DOC or SOC concentration. The SOC adsorption rate onto activated carbon decreases with decreasing initial SOC concentration due to competition by natural organic matter. Equilibrium is achieved after three hours with an initial concentration of 109 μg/L trichlorophenol, yet equilibrium takes twenty-four hours when the initial concentration is 34 μg/L trichlorophenol (Najm*, et al.* 1993). At steady state, activated carbon with a growing microbial colony can remove approximately 40% of the initial DOC from solution by one or more of three independent mechanisms: surface degradation, film degradation, and pore degradation (including in micropores) (Koch*, et al.* 1991). In a test of two carbon types at a Superfund site (wood treatment plant), both carbons had excellent total organic carbon (TOC) removal (minimum 80% removal after 64 bed volumes, influent 320 mg/L TOC). However, the same removal efficiency was not found for waters with an exceptionally high influent TOC concentration (50% removal after 64 bed volumes, influent 900 mg/L TOC) (Dahab*, et al.* 1991) A growing microbial community also is not easily removed during backwashing (Servais*, et al.* 1991).

Pore diffusion appears to control the intraparticle mass transfer rate for DOC with either or both the pore and surface diffusion coefficients being linearly dependent on particle size and with the observed pore diffusion coefficient decreasing over time. Possible reasons for this decrease include the following: (a) the rapid initial diffusion is intraparticle, while the later, slower diffusion is micropore diffusion; (b) the diffusion path length increases as the pores fill; or (c) the displacement of previous adsorbed DOC by more strongly adsorbed DOC causes counter diffusion. Isotherm calculations for DOC sorption onto

activated carbon showed that the percent adsorption after 15 days was nearly identical to that of 7 days. Also, it was determined that for a desired effluent concentration of 1 mg/L DOC ($c_e/c_i = 0.4$), the optimum empty bed contact time (EBCT) was between twenty and thirty minutes (Crittenden, *et al.* 1993).

Excellent removal of phenolic compounds from a groundwater spiked with 20 μg/L trichlorophenol (TCP) has been shown for activated carbon. The maximum adsorption capacity is dependent on the influent sorbate concentration, *i.e.*, capacity and rate of adsorption decrease with decreasing influent concentration (13 mg/L PAC dosage needed one hour contact to reach equilibrium [5 μg/L] while 4 mg/L needed a 24 hour contact time). The adsorption efficiency for a floc-blanket reactor was found to be equal to the adsorption efficiency for batch isotherm tests, indicating that a reactor or filter with sufficient contact time can achieve the maximum removal efficiency for the solute of interest. The adsorption rate of TCP onto activated carbon can be described by the homogeneous surface diffusion model (HSDM) in which an adsorbate molecule first diffuses through the carbon particle's stagnant liquid film layer before instantaneously adsorbing to the carbon's outer surface. The adsorbate then slowly diffuses along the carbon pores' inner surfaces (Najm, *et al.* 1993).

However, the capacity of granular activated carbon (GAC) for phenolic compounds in deionized water is decreased under anaerobic conditions. In the presence of oxygen, the TCP likely is converted to different, unmonitored compounds in the effluent. This results in an erroneously high estimation of adsorptive capacity (Adham, *et al.* 1991). Phenol and *o*-cresol undergo oxygen-induced polymerization reactions on activated carbon that increase both the amount adsorbed and the strength of adsorption. The increases are dependent on the dissolved oxygen (DO) concentration. Seventy percent of the adsorbed phenol was recovered from Filtrasorb 400 activated carbon after adsorption under anoxic conditions while only 25% was recovered after adsorption under aerobic conditions, demonstrating that the adsorption under aerobic conditions led to stronger bonding between the phenol and the carbon. The molecular oxygen aids in the formation of acidic surface oxides on the carbon, which enhances dimer and trimer formation on the carbon surface. The polymerization also significantly increases the time required to reach equilibrium because it is the rate-limiting step. Adsorption is then limited by intracrystalline diffusivity rather than external mass transport resistance. For example, adsorption of phenol on Filtrasorb 400 activated carbon took 48 hours to reach equilibrium under anoxic conditions while it took 14 days to reach equilibrium under aerobic conditions. This increase in adsorption capacity in the presence of dissolved oxygen, however, does not hold for aliphatic organic compounds (Abuzald and Nakhla 1994).

Chlorinated phenols are strongly adsorbed by activated carbon; however, biodegradation of these compounds can also occur on the carbon. Anaerobic degradation of the highly chlorinated phenols, *i.e.*, tetra- and pentachlorophenol, will produce various lower chlorinated phenols, *i.e.*, tri-, di-, and monochlorophenols. This biodegradation and adsorption of the chlorinated phenols will occur simultaneously with pH significantly influencing the adsorption of compounds with acidic functional groups. Batch equilibrium adsorption data for eight chlorinated phenols on Calgon Filtrasorb 400 activated carbon in two concentration ranges at pH 7.0 and 30°C showed the adsorptive capacities increasing from pentachlorophenol to the trichlorophenols and holding fairly constant from the trichlorophenols to the monochlorophenols. The adsorptive capacity for the neutral molecules (monochlorophenols dominant) is higher than that for the ionized forms (pentachlorophenols dominant). The chlorine's position on the phenyl ring, however, has little influence on a chlorophenol's adsorption (Nelson and Yang 1995).

The good fit of the Langmuir isotherm to the adsorption data suggests that a fixed number of accessible adsorption sites exists on the carbon for a given range of solute concentrations. A surface complexation model has been proposed in which the carbon's functional groups can be divided into two types: acidic (carboxyl, phenolic, quinonoid, and normal lactone) groups and basic (chromene and pyrone-like) groups. The surface complexation model fits the adsorption data for 2,4,5-trichlorophenol, 2,4-dichlorophenol, and 4-chlorophenol for different pHs. Tests have shown only slight differences between isotherms for 2,4,5-TCP between pH 4.15 and pH 5.22, but significant differences between the isotherms at higher pH (> 6.5). Solution pH less than the pK_a (6.94 for TCP) does not significantly affect the adsorption capacity of

the activated carbon, but when the pH is greater than the pK_a, there is a linear decrease in adsorption capacity with the increase in pH (Nelson and Yang 1995).

Benzene in groundwater also can be adsorbed on activated carbon. However, this adsorption may be retarded by one or more of the following reasons: fouling of the carbon by various components in groundwater; differences in adsorption and mass transfer kinetics of the various components; adsorption interference and competition by other compounds in groundwater, such as pesticides and herbicides; and interference by chemicals that precipitate on the carbon. At a benzene concentration of 20 mg/L, adsorption may be limited by film diffusion. However, at higher concentrations (50 mg/L), adsorption is not limited by film diffusion because of the larger concentration gradient available, and because pore diffusion controls the rate of adsorption. Bacterial growth on the carbon surface may be either an advantage or a disadvantage. This strictly depends on the microbial population available (Rael, *et al.* 1995).

It has been demonstrated at both a Superfund site and for an industrial wastewater that activated carbon will remove more than one organic compound from a solution. The Superfund site water contained various phenolic compounds (*i.e.*, pentachlorophenol, 4-methylphenol, and 2,4-dimethylphenol), pyrene, fluoroanthene, and unidentified total organic carbon (TOC), and color-producing compounds that were removed from solution by the carbon. However, competitive adsorption led to lesser adsorption efficiency as compared to the efficiency for pure test compounds (Dahab, *et al.* 1991). Competitive adsorption also reduced the capacity of carbon for the individual organics in the industrial wastewater, as compared to their respective single compound isotherms. Capacity reduction can be correlated with the percent of the total organic carbon (%TOC) in solution contributed by the target compound, *i.e.*, the smaller the %TOC, the larger the capacity reduction, because other compounds are available in sufficient concentration to compete for many of the adsorption sites. Mass transport limitation also can significantly reduce a compound's adsorption capacity, especially for large organic contaminants such as color agents (Ying, *et al.* 1990).

Activated carbon also can remove pesticides from solution. Atrazine and two of its degradation products, deethylatrazine and deisopropylatrazine, have been adsorbed from contaminated groundwater (200 μg/L atrazine filtered at 5 mL/min for 70 days through a 2 cm ID x 30 cm long filter column) (Selim and Wang 1994). A sand filtration/carbon treatment system can reduce a diversity of organophosphate, organochlorine, and pyrethroid pesticide residues down at least to their detection limit. The sand filtration step removes the pesticides associated with particulate matter while the carbon adsorbs the nonparticulate pesticides in the solution. Average removal efficiencies for the total treatment system were 79% for pyrethroids, 92% for organophosphates, and 96% for organochlorines (Moore, *et al.* 1985). Activated carbon filters also can provide a good environment for microorganisms that may biodegrade certain organic molecules. The biodegradation often will increase the apparent adsorptive capacity of the carbon (Selim and Wang 1994).

Inorganic (Non-Metal) Removal Capability
Activated carbon fiber has been shown to remove iodine and iodide compounds from acetic acid in water, methanol, and ethanol solutions. When compared to other conventional adsorbents (activated carbon, silica gel, alumina, NaY zeolite, Ag ion-exchanged NaY zeolite, and Ag ion-exchanged Amberlyst XN 1010), the activated carbon fiber had the greatest adsorptive capacity for the iodine and iodide compounds. Iodine removal was inversely related to iodine's solubility in the solution. The excellent removal by the fiber can be explained by the unique structural characteristics of activated carbon fiber which promote fast adsorption. Since the fiber contains only micropores with a pore diameter less than 2 nm while activated carbon has a broader pore size distribution, the adsorptive capacity is greater for the fiber. This is because the major (stronger) adsorption sites are located only in the micropores with weaker adsorption in the meso- and macropores. Iodine diffusion to the strong binding sites is the rate-limiting step in activated carbon adsorption; this diffusion is eliminated in the fiber because the micropores are on the surface (Yang, *et al.* 1993).

Activated carbon also can reduce chlorite ions to chloride by having the oxychlorine species react with the radical sites, oxygen-containing functional groups, and metal ions on the activated carbon to form the radical entities ClO_2, Cl^o, and ClO^o. These then form Cl_2O_2, Cl_2O_3, HOCl, etc. with chloride, chlorate ions, and oxygen as final products. Increasing the initial chlorite concentration increases carbon's adsorption capacity for other compounds because the chlorate-forming secondary reactions are favored which increases the concentration of acidic surface functional groups, thus increasing the number and type of sites available for adsorption by not only chlorite but also other compounds. One gram of granular activated carbon removed 600 mg/L of chlorite from solution (Vel Leitner, *et al.* 1994).

The presence of phenol or *p*-nitrophenol in solution or preadsorbed on carbon, however, will decrease its capacity to remove chlorite because many byproducts, such as chlorophenols, *p*-benzoquinone, dimerization, and carboxylation products, are formed on the carbon surface once the chlorite contacts the organics. These halogenation reactions occur in the granular activated carbon (GAC) bed both when the chlorite is in solution with the organics and when the chlorite-free organic solution is passed over chlorite-preoxidized activated carbon. Oxidation of activated carbon with chlorite apparently promotes the catalytic properties of the carbon surface. Other disinfectants such as NH_2Cl, Cl_2, ClO_2 also undergo halogenation reactions with organics in the presence of activated carbon. These byproducts may be less desirable than the organics originally in solution. Some of the byproducts formed from reactions of organics and disinfectants on the activated carbon surface include aromatic acids (benzoic acid, salicylic acid, hydroxynitrobenzoic acid, and nitrobenzoic acid), benzaldehyde, hydroxybenzaldehyde, 4-phenoxyphenol, 4-phenoxymethoxybenzene, 2,2'-dihydroxybiphenyl, benzofuran, 2,3-benzofurandione, chloronitrobenzenes, and nitrosophenol (Vel Leitner, *et al.* 1994).

Metal Removal Capability
Hexavalent chromium is effectively removed by a pH-dependent adsorption with the peak adsorption at pH 6 (Sharma and Forster 1993). More than 80% of inorganic and organic mercury in a solution has been removed by a commercial granular activated carbon, with even greater removals resulting when humic acid or nitrilotriacetic acid (NTA) was added to the solution (initial solution, 10 μg/L Hg(II) and 5 mg/L of humic acid or NTA). Activated carbon from peanut shells is seven times more effective than commercially-available activated carbon at the removal and recovery of mercury from solution, possibly because the peanut hull carbon has a higher moisture content that may increase its porosity and makes available more sorption sites. Peanut hull carbon also has a lower ash/higher carbon content (70 mg peanut hull carbon for adsorption of 20 μg/L in 100 mL solution versus 500 mg commercially available activated carbon for the same adsorption). Peanut hull carbon has lower decolorizing capacity and a moderate ion-exchange capability as compared to the commercially available carbon, implying that it will not be as suitable for organic adsorption. Peanut hull carbon adsorption also is not as pH dependent as commercially-available activated carbon. Rice-husk and coconut-shell activated carbon also has been effective in the removal of heavy metals from aqueous solutions. The adsorption process follows both the Freundlich and Langmuir isotherms with pore diffusion being only one of the rate-controlling steps (Namasivayam and Periasamy 1993).

Microorganism Removal Capability
Historically, it has been believed that silver-impregnated activated carbon rendered bacteria inactive, *i.e.*, made drinking water 'safer,' possibly because low pH, lower temperatures, higher mineral matter, and phosphate concentrations could reduce bacterial action. Testing of a commercial silver-impregnated carbon filter showed that the concentration of *Salmonella typhi* was reduced more than 5 logs (99.999 percent) at a silver concentration of 50 μg/L and 1 hour of exposure; however, the concentration of *Pseudomonas aeruginosa* was reduced less than 50% and the concentration of *poliovirus type 1* was not reduced under the same conditions. Under most circumstances and with long-term use, the silver-impregnated activated carbon filters have negligible ability to remove microorganisms from solution (Bell 1991). Silver has been fused into activated carbon and some ceramic filters in order to prevent biofilm growth in some household water filtration units, e.g., Katadyn water filters.

Other Carbon-Based Filters

Carbonaceous residues such as wheat straw have been used to remove nitrogen from reclaimed wastewater in a nitrification/denitrification sequence. The wheat straw is then a source of carbon for the microbial colonies that perform the nitrification and denitrification. The straw's capacity for nitrogen, ammonia, and nitrate immobilization was found to be about 9 mg N/g (mg nitrogen per gram). Significant reductions in BOD, organic carbon, chlorophyll, phosphorus, algae, and clay concentrations in the influent were also found (Lowengart, *et al.* 1993). The wheat straw substrate has a poor nutrient content that leads to the removal of nitrogen and phosphorus from the influent water by the microbial biomass (Diab, *et al.* 1993).

Ultrafiltration membrane pores (0.001 - 0.1 μm) are relatively large and can remove only those molecules and particles that are larger than the pores. Inorganic ions readily pass through these membranes. Activated carbon has been added to ultrafiltration systems in order both to remove the organics that cause early clogging of the filter and to sorb many compounds that would pass through the filter. The activated carbon concentration should be less than 600 mg/L for the best operational efficiency. Powdered activated carbon (PAC) is usually used in conjunction with ultrafiltration membranes because the smaller particle sizes of the PAC have considerably faster adsorption kinetics and reduce the required contact time. As with all activated carbons, the carbon concentration required to achieve a particular effluent concentration is directly related to initial concentration of the contaminant in question (Adham, *et al.* 1991).

Limitations of Activated Carbon

Activated carbon cannot desorb high boiling solvents and will polymerize or oxidize some solvents to toxic or insoluble compounds (Blocki 1993). It has a very small net surface charge and is ineffective at removing free or hydrated metal ions, unless they are complexed with easily-adsorbed organics prior to filtration. However, once they are complexed with these insoluble organics, the complexed metals are readily adsorbed onto the carbon, which result in the desired high removal rates (Anderson and Rubin 1981).

Peat Moss

Peat is loosely defined as partially decomposed organic material, excluding coal, which is formed from dead plant remains in water in the absence of air. The physical structure and chemical composition of peat is determined by the types of plants (mosses, sedges and other wetland plants) from which it is formed. Peat is physically and chemically complex and is highly organic with its main components being humic and fulvic acids and cellulose.

Peatland development is controlled by several processes, including peat accumulation, *Sphagnum* acidification, and climate. The general movement from rich to poor fen and then to bog is primarily a result of peat accumulation. Peatland development can range from <1500 years to >2000 years and usually occurs in areas with gentle topography and where the prevailing climate has short, warm, moist summers and long, cold winters. Bogs and poor fens are *Sphagnum*-dominated while rich fens contain mostly brown mosses (Kuhry*, et al.* 1993).

Peat accumulation causes the land surface to become separated from the mineral-rich ground water, i.e., the depth to the water table increases. Mesotrophic rich fens develop into oligotrophic poor fens that are further acidified by *Sphagnum*. Continued peat accumulation results in the development of ombrotrophic bogs, which depend exclusively on precipitation for nutrients and water. The rapid transition from rich fen (pH > 6) to poor fen and bog (pH < 5) is most probably a result of chemical factors, *i.e.*, the 5 - 6 pH transition range is also where the bicarbonate alkalinity becomes zero. Once this bicarbonate buffer is gone, the peatland is very sensitive to further oligotrophication and *Sphagnum* acidification. The removal of regular contact with the deeper, mineral-rich ground water also reduces the opportunity for neutralization of the acidification caused by *Sphagnum* (Kuhry*, et al.* 1993).

Peat Composition

Peat contains the products of inhibited plant and vegetable matter decomposition and may contain up to 15% bituminous substances, including a wide range of saponifiable (*e.g.*, C_{18}-C_{30} free fatty acids, fatty acid triglycerides, and non-glyceride esters) and unsaponifiable liquids (*e.g.*, long-chain hydrocarbons, alcohols, and steroids). At ambient temperature, the peat bitumen is a solid-liquid system. The solid phase consists of several different crystalline species of carboxylic acids and esters while the liquid phase is highly viscous and consists of a mixture of paraffins, carboxylic acids, alcohols, and esters. The flow behavior of the bitumen is similar to that of a yield pseudoplastic fluid. The behavior is extremely temperature sensitive because of both the melting and crystallizing of the crystalline minerals and the changing polar interactions in the non-crystalline component. At ambient temperature using polarized light microscopy, the bitumen was found to contain many small crystallites (diameter, 5.4 μm). Using successive organic extraction steps, the peat bitumen was found to contain wax (43.9%), resin (37.9%), and asphaltene (6.7%) with the remaining 11.5% containing some visible peat fibers but probably consisting mostly of polymerized peat fatty acids and hydroxy acids. Infrared spectroscopy indicated that the polar species such as esters and acids are primarily in the wax and asphaltene fractions, while the resins consist largely of non-polar constituents (Leahy and Birkinshaw 1992).

Carboxylic acids and esters in the wax fraction likely are the dominating rheological influence in the bitumen. They affect the peat's physical behavior because they crystallize at a low temperature and mechanically hinder flow, and because their secondary bonding increases the liquid's viscosity. The crystallizing species appear to be the esters of the fatty acids rather than the more polar acids, possessing molecular weights below 1200 (Leahy and Birkinshaw 1992).

While the wax consists primarily of medium and high molecular weight species, the liquid resin is almost completely low molecular weight material, such as paraffinic liquids, and carbonyl and hydroxyl species. No aromatic or unsaturated species appear to be in the resin. The paraffinic liquids are non-crystalline, with flow characteristics, at ambient temperature, of a low-viscosity Newtonian fluid. As the crystallinity of the resin increases, the flow becomes yield pseudoplastic (Leahy and Birkinshaw 1992).

The asphaltene fraction appears to consist of similar-sized species to those in both the wax and the resin but is believed to contain more polar constituents. The crystallizing species in the asphaltene are of relatively high molecular weight; however, analysis of the asphaltene indicates that low molecular weight species are present and dilute the crystallizing species. The first fraction of the asphaltene on an infrared spectra is a paraffin, followed by mixtures of saturated acids and esters, with esters. Acids increase in significance and concentration in the later fractions. The largest-sized fractions of the asphaltene appear to contain several unsaturated compounds (Leahy and Birkinshaw 1992).

Hydraulic Characteristics

Peat moss (*sphagnum* moss) is a fibrous ("fibric") peat and is typically brown and/or yellow in color. It has easily identifiable undecomposed fibrous organic materials, and its bulk density is generally less than 0.1 g/cc. Because of its highly porous structure, peat moss can have a high hydraulic conductivity, up to 140 cm/hr. (Galli 1990). Its chemical and physical structure (pore volume of 80-90% [Karamanev*, et al.* 1994]) encourages water retention, and it can contain up to approximately 90% water by weight (Leahy and Birkinshaw 1992). Peat permeability varies greatly and is determined both by its degree of decomposition and the plants from which it came. A 50% change in a peat's moisture content can change its permeability up to five orders of magnitude (Mitchell and McDonald 1992). Generally, the more decomposed the peat is, the lower its hydraulic conductivity. Peats lose most of their hydraulic conductivity when compressed. Two different flow regimes exist in peat filters because of the peat's three-level, fractal-like structure, *i.e.*, the same shape of the structure is observed at three different magnifications. At low velocities, the liquid flows through the peat moss particles; however, at high velocities (above the critical velocity of approximately 0.1 cm/s), the liquid mainly flows between the solid aggregates with only a small amount penetrating the particles forming the aggregates. The mass transfer mechanisms appear to be due to the following: 1) diffusional transfer at the smallest level; 2) convective or diffusional transfer (or both) at the second level, depending on the liquid velocity; and 3) convective transfer at the largest level (Karamanev*, et al.* 1994).

Peat moss' coarse structure likely causes the observed decrease in hydraulic conductivity as the water content is reduced. Peat also exhibits a hysteresis between the drying and wetting curves, likely because as the material dries out it becomes more hydrophobic and, consequently, more difficult to rewet (da Silva*, et al.* 1993), with severely dried peats (>= 35% moisture loss) being exceptionally difficult to rewet. Possible reasons for this phenomenon include macropore collapse and high micropore suction-pressures. Drying also shrinks humic molecules, binding the color-producing, lower-molecular-weight fractions together. The peat initially will repel new water; however, continuous rewetting eventually will lead to water penetrating all pore spaces, saturating the peat, and flushing out any accumulated color-producing organic acids (Mitchell and McDonald 1992).

Natural peaty clays have a high organic content (>20%) and are compressible because of void volume in the mix. However, amendment of the peat with sand can greatly reduce its compressibility, which also will increase its bulk density and decrease its moisture content. When the sand to peat ratio is 1.76, the bulk density of the mixture increases from 1,310 kg/m^3 to 1,776 kg/m^3, and the moisture content decreases from >80% to 23% (Lo*, et al.* 1990).

Organic Removal Capability

Peats can extract substantial amounts of either free-phase or dissolved hydrocarbons from water (between 50 and 90% of the starting wet volume and 63 and 97% of dissolved hydrocarbons from saturated solutions). In general, the best peats for hydrocarbon adsorption are low in fiber and birefringent organics and high in ash and guaiacyl lignin pyrolysis products. Because these parameters indicate the degree of peat decomposition, adsorption appears to increase as decomposition increases, possibly for the following reasons: (1) greater surface areas are associated with smaller particles; (2) chemical changes resulting from decomposition; or (3) inherent chemical or physical differences in the source plants. Sorption possibly results from the aromatic surfaces attracting the hydrocarbon while cross-linking side chains "trap it" and hold it in place. Another potential explanation of hydrocarbon

sorption to peat is that the intermolecular distances and area within the lignocellulosic polymer are suitable for absorption between basal lignin units. Inter- and intra-molecular forces between the lignin and the hydrocarbon control the competition between the two mechanisms (Cohen, *et al.* 1991).

Toluene is sorbed more slowly to peat than either benzene or *m*-xylene, yet toluene had much less variation in its sorption to different peat types than benzene and *m*-xylene. With sufficient contact time, toluene sorption capacity is similar to that of benzene and *m*-xylene. In free-phase experiments, the absorbencies exhibited by the specific peat types did not depend on the type of hydrocarbon sorbed, with the Maine *sphagnum* peat having somewhat less absorption per unit volume than other peats. This may be a result of the visibly larger pore size in *Sphagnum* peat compared to other peats. *Sphagnum* has more visible, preserved fibers, a higher water-holding capacity, and a relatively high porosity, which, along with pore size, type, and shape, may be significant factors in hydrocarbon adsorbency (Cohen, *et al.* 1991).

Peat moss can, however, shrink or swell in the presence of some organic compounds, possibly because sorption site availability increases in liquid sulfoxides, with the increase being dependent on humification despite the general decrease in oxygen/carbon ratio with humification. Swelling and/or shrinkage of the peat has been demonstrated by sorption of pure (>95%) methyl, tetramethylene, and propyl sulfoxides and propyl sulfones on dewaxed, acid-form peats. Apparently, the cellulose particles adhere to one another when dry. The addition of a liquid, even a nonswelling one, lubricates the particles so that initially they compact slightly (Lyon 1995).

Alcohol sorption curves are similar, even with large differences in humification between the two peats studied, implying that the alcohol sorption sites within peats are not changed significantly by humification. Significant swelling was observed for peats immersed in propyl sulfoxide, demonstrating that the approximate limit of swelling, as found by Lyon and Rhodes, by solvents with molar volumes $\leq$ ca. 93 cm^3 mol^{-1}, can be exceeded when the liquid contains a strongly interacting functional group. The swelling limit for most alcohols is probably influenced more by the peat's basic sites rather than the acidic sites, and, therefore, different limits are possible for acidic and basic organic liquids (Lyon 1995).

The binding of polycyclic aromatic hydrocarbons (PAHs) to both solid soil humic materials and dissolved humic substances appears to be controlled by both adsorption and partitioning with the filter media, with the partitioning term being the most important for largely nonpolar sorbates. The sorption of phenols and PAHs correlates well with their hydrophobicity. The sorption of nonpolar organics correlates well with the oxygen content of the organic matter in the peat, with the exception of a few polymers that have a high oxygen content. Nitro and hydroxyl groups on a sorbate molecule tend to strengthen the molecule's sorption because of the charge transfer interactions that occur between the sorbate and the peat. The correlation between a nonpolar organic's hydrophobicity and sorption capacity is not valid for aromatic amines where sorption exceeds the estimated bonding by five to ten times. The number of aromatic rings also appears to influence sorption capacity significantly. Fulvic acids are slightly more polar than humic acids, and, thus, they are slightly more water soluble and have slightly different sorption capabilities (Kopinke, *et al.* 1995).

Peat can also leach organic compounds, especially colored organic matter such as humic and fulvic acids. The amount of leaching of colored compounds is dependent upon season (for an outdoor filter) and soil moisture. One possible explanation for the correlation of peat moisture and color distribution and intensity is the change in pH and water content during filtration. The peat showed a rapid initial rise in color and pH/acidity, followed by a gradual decline. The length of drying between filtration events indicates the size of the "store" of water-soluble, color-producing organic acids, especially in the top 3 cm where aerobic decomposition and oxidation also is occurring. When the filter is initially wetted, this "store" is released, and the effluent becomes colored as the decomposition products come into contact with water and become 'color' (Mitchell and McDonald 1992).

Inorganic (Non-Metal) Removal Capability

A peat-filter system has been developed for enhanced nitrogen removal or transformation in sanitary wastewater. The filter uses a layer of *sphagnum* peat moss placed below the weeping tile bed where nitrogen is assimilated into the fungal biomass, thus reducing the nitrogen content of the wastewater. Sixty to 100 percent removals have been achieved for nitrate levels up to 125 mg N/L (Robertson and Cherry 1995). Peat is an excellent substrate for microbial growth, with large colonies of nitrifying and denitrifying bacteria typically present. It can assimilate nutrients and organic wastes because of its high C:N:P ratio, which often approaches 100:10:1. Long-term phosphorus retention in peat is related to its calcium, aluminum, iron, and ash content with the higher the content of each of the above constituents, the higher the retention capability (Galli 1990). A peat filter system for treating septic tank effluent has been able to treat wastewater at a hydraulic loading rate of 40 L/m^2 of filter surface while maintaining a high effluent quality: NO_3-N (<5 mg/L), NH_3-N (0 - 17 mg/L), organic-N (0 - 7 mg/L), BOD_5 (5 - 20 mg/L), DO (3 - 13.3 mg/L), TSS (5 - 15 mg/L), pH (5.3 - 6.5), and fecal coliforms (reduced by 99.99+ %). The major drawback to the system was the tea color of the effluent (Daigle 1993).

Metal Removal Capability

Because of the lignins, cellulose, and humic and fulvic acids in peat, peat is highly colloidal, is polar, has a high cation-exchange capacity, and has a high specific adsorption capacity for transition metals and polar organics (Galli 1990). *Sphagnum* moss contains an anionic polysaccharide ('sphagnan') that selectively binds calcium and other multivalent metal cations. As the dead moss slowly becomes peat, soluble sphagnan is gradually released. However, sphagnan is unstable, and in the mildly acidic conditions of peatland formation, it is slowly converted into humus or humic acid. Humic acid also binds multivalent metal cations, and its selectivity for Ca^{2+} is even higher than that of sphagnan, thus ensuring that peatlands are permanently decalcified (Painter 1991).

Peat moss has been used to treat metal-bearing industrial effluents since it will adsorb, complex, or exchange various metal cations (Gosset*, et al.* 1986). Peat has an excellent natural capacity for ion exchange with copper, zinc, lead, and mercury, especially at pH levels between 3.0 and 8.5. The peat contains polar functional groups such as alcohols, aldehydes, ketones, acids, and phenolic residues which chemically bind metal ions from a solution (Sharma and Forster 1993). However, the sorption capacity of peat is finite and reversible and is controlled by the pH of the solution (Galli 1990).

Immobilization of a metal by peat depends on (i) the metal ion capture chemistry, (ii) solute transport rates from the bulk solution to the adsorbent surface, and (iii) the transport rates and equilibria within the adsorbent's interstices. For metal adsorption on peat, film diffusion appears to be the rate-controlling step; although at small peat-to-metal ratios, internal mass transfer also greatly influences the sorption. A three-step model can be used to describe the metal immobilization process by peat: (i) solute mass transfer from the solution to the particle surface, (ii) ion-exchange reactions at fixed sites on the peat, and (iii) internal diffusion of solute. In general, the ion-exchange reaction is very fast compared to the other two steps and is not the kinetic rate-limiting step. At high peat concentrations, film and external mass transfers are most important while at low peat concentrations, intraparticle diffusion controls the reaction rate (Allen*, et al.* 1992).

In buffered solutions, the order of sorption for four metal ions to peat is $Ni^{2+} > Cu^{2+} > Cd^{2+} = Zn^{2+}$, independent of peat origin. Above pH 3, copper binding is similar to nickel and is dependent upon the pH of the solution; cadmium and zinc present a similar pH dependence but are less strongly bound than the copper and nickel. Only the nickel cation, however, is bound strongly enough not to be desorbed when the pH is dropped to below 1.5 (Sharma and Forster 1993).

In unbuffered solutions, the pH drops between 0.2 and 0.6 pH units during filtration for all metal-peat combinations tested (Gosset*, et al.* 1986) because of the release of humic and fulvic acids during adsorption or ion exchange (Sharma and Foster 1993). Unsieved and non-acidified oligotrophic or eutrophic peat samples seem to bind copper more rapidly and efficiently than sieved and acidified ones, possibly because the structure of the peat is changed during acid pretreatment. The sorption curves for

the metals are not linear, regardless of the peat-metal combination, indicating that the peat-metal complex stoichiometry and thermodynamics are probably dependent both on the free metal concentration and on pH, which varies in unbuffered solutions. Although saturation limits of 200 mmol metal/kg dry weight peat were observed in buffered solution, sorption saturation (even at 0.1 M metal in 50 g/L peat) was not observed in unbuffered solutions. Maximum removal could be achieved when the metal concentration in the buffered solution was in the 0.1 - 1 mM range, provided that there is adequate contact time (Gosset, *et al.* 1986). *Sphagnum* moss has been shown to remove iron (75% reduction) and manganese (25%) from acid mine drainage in Pennsylvania ("Moss Tested to Remove Manganese from Mine Drainage," 1984).

Sphagnum moss peat concentrations ranging from 4 to 40 g/L can effectively remove hexavalent chromium from solution (10 to 1000 mg/L Cr(VI)), especially when the ion concentrations are low. At equilibrium pH of 2.0, almost complete removal of Cr(VI) can be achieved when chromium concentrations are less than 100 mg/L, while at equilibrium pH of 1.5, 64% Cr(VI) removal can be achieved when chromium concentrations are less than 1000 mg/L. The sorption is pH dependent, with the optimum range being 1.5-3, and is controlled by (i) chemical reduction, *i.e.*, Cr(VI) to Cr(III); and (ii) adsorption of the mainly Cr(VI) species. The chromium is strongly bound, and little desorption occurs in low molarity caustic solutions. In high molarity caustic solutions, the peat itself 'disintegrates' (Sharma and Forster 1993).

Limitations of Peat Filters
The release of color upon wetting is one problem with peat. Another potential problem is that peat may leach some nutrients, depending on the soil and water chemistry and water level. *Sphagnum* peat generally will release significantly more phosphorus and ammonium than *Carex* peat with the water quality determining the extent of nutrient release, especially in waters with a high sulfate concentration. Temperature also influences the amount of ammonium, potassium, and phosphate leached. Nutrient leaching will increase two to three fold after the peat has been frozen (Koerlsman, *et al.* 1993).

Stormwater Runoff Treatment
Urban road runoff generally has large concentrations of heavy metals and particulate organic carbon, as well as high alkalinity. Peat moss has been used as a growth medium for plants, such as red maple and cranberry seedlings, to treat urban stormwater runoff containing lead and zinc. In general, metals in acidic swampwater were more available to the plants than those in alkaline runoff and uptake of the metals usually increased with decreasing pH and decreased with increasing soil organic matter content. However, soluble organic acids can mobilize heavy metals into solution, even those in alkaline runoff water (Vedagiri and Ehrenfeld 1991).

Peat-sand filters (PSF) have been proposed to treat urban runoff. The PSF is an aerobic, "man-made" filtration system, unlike older sand or peat filtration systems that use naturally occurring soils as the filter. The peat-sand mixture layer must be manufactured, as it does not occur in nature. A PSF can be expected to remove most of the phosphorus, BOD, and pathogens, and with a good grass cover, other nutrients (Galli 1990).

The Peat-Sand Filter System designed by the Metropolitan Washington Council of Governments (Washington, D.C.) would have a good grass cover on top underlain by 12 to 18 inches of peat. The peat layer is supported by a 4-inch mixture of sand and peat that is supported by a 20- to 24-inch layer of fine to medium grain sand. Under the sand are gravel and the drainage pipe. The mixture layer is needed because it will provide the necessary continuous contact between the peat and the sand layers and ensure uniform water flow. Because the PSF is a biological filtration system, it will work best during the growing season when the grass cover can provide the additional nutrient removal that will not occur in the rest of the filter (Galli 1990). The expected pollutant removal efficiencies are given in Table 14.

Table 14. Peat-sand filter pollutant removal efficiencies (Source: Galli 1990)

Pollutant	Removal Efficiency (%)
Suspended Solids	90
Total Phosphorus	70
Total Nitrogen	50
BOD	90
Trace Metals	80
Bacteria	90

Compost

Composts made from yard waste, primarily leaves, have been found to have a very high capacity for adsorbing heavy metals, oils, greases, nutrients, and organic toxins due to the humic content of the compost. These humic compounds are stable, insoluble, and have a high molecular weight. They act like polyelectrolytes and remove the toxicants from the runoff either by adsorption or ion-exchange. The exact content of and aging process for the composts used by W&H Pacific/CSF Systems, Inc. are not public knowledge with the result that the filter installation-and-maintenance company supplies the compost to the stormwater treatment device owner.

The composted leaf filter was developed by W&H Pacific for Washington County (WA), the Unified Sewer Agency, and the Metropolitan Service District of Washington County (W&H Pacific 1992a). The filter consists of a bottom impermeable membrane with a drainage layer above it. Above the drainage layer is a geotextile fabric upon which rests the compost material. The actual toxicant removal occurs in the compost layer by filtration, adsorption, ion exchange, or biodegradation, or by a combination of these processes.

The composted leaf filter is advertised as an improvement over other stormwater treatment devices, such as detention ponds and grass swales, because the square footage required for the filter is much smaller than for the other devices. A small presettling area (less than one minute detention time) is recommended; otherwise, the larger particles and floatables will prematurely clog the filter and reduce its treatment efficiency. Filter design was based on permeability tests performed by W&H Pacific and the design flow was selected as 2.25 gallons per minute (0.30 m^3/min), which gives a required compost bed surface area of 200 ft^2/cfs (60,435 m^2/m^3/sec.). The results from the testing of a prototype Compost Storm Water Filter System (CSF) are given in Table 15. This filter was located where the drainage area is 74 acres (3.9 acres highway, 70 acres mixed residential).

A three-year testing program on the CSF has shown that the filter is excellent at removing metals and hydrocarbons from the runoff. Sediment accumulation, always a potential problem for any filtering system, was, during the 1992-93 testing season, approximately 74 ft^3 (2.1 m^3) with an average thickness range of 0.25 to 1.27 ft (0.07 to 0.4 m). During the 1993-94 season, 111 ft^3 (3.1 m^3) of sediment with an average thickness of 0.5 to 1.2 ft (0.14 to 0.4 m) collected in the system (CSF Systems 1994). Based upon the sample results at the location of the compost filter, the first flush of a storm had the heaviest pollutant loadings, and the filter had the highest removal efficiencies during this first flush. This indicates that the CSF System is capable of treating a shock loading of pollutants while producing an acceptable effluent. The average first flush removal rates for the three years of operation are given below in Table 16.

CSF Systems, Inc., the manufacturer and distributor of the compost filter, outlines the advantages and disadvantages of this compost system. One advantage is that the filter has a very high buffering capacity in the alkaline range. When the influent is between pH 6.7 and 8.3, the effluent is consistently between pH 7.0 and 8.0. However, because the media acts as an ion-exchange resin, whenever a pollutant sorbs to the media, an ion is 'leached off.' In the case of the compost, soluble phosphorus is one of the ions that is leached off during ion exchange (influent, 0.09 - 1.0 mg/L; effluent, 0.29 mg/L). Soluble phosphorus likely is released from the captured solids through microbial action and since the compost only has a weak anion exchange capacity, most of the soluble phosphorus is not removed from the water once it is leached from the compost. Testing has also shown an increase in boron and nitrate in the effluent of the compost filter (CSF Systems 1994).

Table 15. Compost filter pollutant removal efficiencies (Source: CSF Systems 1994)

Pollutant	Influent/Effluent Concentration Range	Removal Rate (%)
Turbidity		82
Total Solids		49
Suspended Solids		92
Total Volatile Suspended Solids	0-90 mg/L Influent; 0-14 mg/L Effluent	89
COD		70
Settleable Solids	0-4 mL/L Influent; 0.05-0.1 mL/L Effluent	95
Total Phosphorus		49
Ammonia		60
Total Kjeldahl Nitrogen		57
Copper		7
Zinc		83
Lead		83
Aluminum		84
Iron		91
Petroleum Hydrocarbons		84
Oil and Grease		81

Table 16. Compost filter removal efficiencies – first flush (Source: W&H Pacific 1992b; CSF Systems 1994)

Pollutant	Removal Rate (%)
Turbidity	86
Total Solids	63
Total Suspended Solids	94
Settleable Solids	98
Total Volatile Suspended Solids	97[*]
COD	79
Total Phosphorus	63
Ammonia	65
Total Kjeldahl Nitrogen	72
Copper	83
Zinc	86
Lead	86
Aluminum	88
Iron	93

* Results are from the first year of operation only.

Zeolite

Adsorbents must be sufficiently selective and have adequate capacity and stability to achieve the required separation economically over a prolonged period of time. To get the required capacity, the adsorbent must have a high specific surface area, *i.e.*, be highly porous with fine pores (micropores). Furthermore, most important adsorbents use physical adsorption (multilayer) rather than chemisorption in which the capacity is limited to monolayer coverage (Ruthven 1988). Zeolites are preferred as adsorbents in the chemical process industry because they are inorganic, non-flammable, and can withstand very high temperatures (Vaughn 1988). Generally, they are porous aluminasilicates which may occur naturally but also can be synthesized (Blocki 1993). They have been used in such diverse applications as natural gas purification (chabazite), radioactive waste disposal (clinoptilolite), ammonia recovery from sewage effluents (clinoptilolite), and various petroleum and petrochemical catalyst applications (erionite, mordenite) (Vaughn 1988).

Physical Characteristics

Zeolites occur naturally in basaltic lava, in specific rocks subjected to moderate geologic temperature and pressure, and in altered and reacted volcanic ash deposits (Vaughn 1988). Clinoptilolite is the most abundant naturally occurring zeolite. The formula of one cell of clinoptilolite is $(Ca,Na_2,K_2)_3[Al_6Si_{30}O_{72}] \cdot 24 \, H_2O$. It has a two-dimensional 8-ring and 10-ring channel structure with the largest cavity measuring 4.4 x 7.2 Å. Zeolite surface chemistry is similar to that of smectite clays with the difference between the two being that natural zeolites may be millimeter or greater sized particles and do not exhibit shrink-swell behavior (Haggerty and Bowman 1994).

The primary building block of zeolite is a tetrahedron of four oxygen atoms surrounding a central silicon atom $(SiO_4)^{4-}$. Zeolite polyhedra are connected by shared oxygen atoms on the corners, and these polyhedra connect to form the various specific zeolite crystal structures. Different combinations or arrangements of the same polyhedra may give numerous distinctive zeolites. Other elements, such as Al, Ga, Ge and Fe (Haggerty and Bowman 1994), may be substituted for the silicon, provided that they "fit" into the center of the four tetrahedral oxygen atoms without too much strain on the oxygen bonds and that the resultant structure is electrically neutral (Vaughn 1988). Union Carbide scientists in alumino-phosphate chemistry recently have expanded zeolite compositions to include about 13 elements, including Li, Be, B, Mg, Co, Mn, Zn, P, As, and Ti (Haggerty and Bowman 1994). These variations in the chemistry in the basic structure change the pore sizes available for sorption and therefore alter the selectivity that can be achieved by a zeolite (Blocki 1993).

Zeolites often are called molecular sieves because their crystalline framework has channels (pores) and interconnecting voids of molecular size (3 to 10 Å) (Vaughn 1988). Zeolite species are often specified by letters after their name. Zeolite A has 8-member oxygen rings with a void size of 4.3 Å in the Ca^{2+} form, 3.8 Å in the Na^+ form and 3.0 Å in the K^+ form. X and Y zeolite pores, both of which have 12-member oxygen rings and whose frameworks are identical, are larger, having a free aperture of about 8.1 Å. The difference between the X and Y zeolite is the Si/Al ratio which controls the cation density and therefore affects its adsorptive properties. The zeolite with the intermediate pore size has a 10-member oxygen ring and has a pore size of about 6.0 Å (Ruthven 1988). The ability to control access to the reactive sites by selecting the zeolite with the pore size in the desired range, as well as the size and stereochemistry of the site itself, makes molecular-level control of chemical reactions possible (Vaughn 1988).

Zeolite Synthesis

Zeolite synthesis is usually a batch process run at one of the following conditions: (1) 90-100°C, 1 atm. pressure, pH > 10; (2) 140-180°C, 5 - 10 atm., pH > 10; or (3) 100-180°C, water + "amine" autogenous pressure, pH > 10. The metal phosphates, a relatively new class of zeolites, are made under conditions similar to (3) above, except that the pH is between 3 and 6 (Vaughn 1988). By varying the chemistry in the basic structure, different pore sizes and different selectivities can be achieved (Blocki 1993).

Once the crystal synthesis is complete, the zeolite is mixed with a binder, and then formed into beads, pills, tablets, or extrudates. In most applications, the binder must be completely inert to avoid side reactions. Fabrication of the zeolite pellet is difficult because one must avoid plugging the pores with the binder and must avoid crushing the crystalline structure in high-pressure pilling processes. Most applications require maximum activity or sorption capacity, and, therefore, the manufacturing process tries to maximize zeolite content and minimize binder content (Vaughn 1988).

Zeolite Adsorption/Ion-Exchange Characteristics

Because micropore size is uniform in zeolites, these adsorbents have a rather sharp cut-off of sorption with increasing molecular size. Although the framework primarily determines the pore size, the free aperture, particularly in the smaller 8-ring sieves, may be modified by ion exchange, again tailoring the zeolite to a specific effective pore size. Zeolite also is a polar molecule, and it has some unique affinities that are promoted by the ability to fit a particular molecular shape into a pore. These features also contribute to the ability of zeolite to be a highly selective adsorbent. Adsorption forces for zeolites can be divided into van der Waals forces, induced dipole interactions, and other electrostatic forces (polarization, dipole and quadrupole interactions). Van der Waals forces affect any sorbate-sorbent pair because they depend on the surface (micropore) geometry and increase with the polarizability of the sorbate molecule. Molecules which just 'fit' in the pore channel have maximum van der Waals interaction energy. By contrast, electrostatic forces, except for polarization energy, require both a surface electric field, *i.e.*, polar or heterogeneous adsorbent, and a dipolar or quadrupolar sorbate molecule (Ruthven 1988).

When Al^{3+} is substituted for Si^{4+} in the zeolite framework, a net negative charge on the molecule results. This is compensated for by a 'nonframework' cation (*e.g.*, Na^+), which is 'held' in the pores of the structure. Because this cation is not a part of the crystalline lattice, it is relatively mobile and easily exchangeable for other cations (Vaughn 1988). Ion-exchange and adsorption processes for zeolites often are even more complicated than for organic ion-exchange resins because the zeolite has two distinct pore structures: micropores in the crystals and macropores in the binder, both of which can participate in sorption (Robinson*, et al.* 1994). Zeolites have internal and external surface areas of up to several hundred meters squared per gram. They can have cation-exchange capacities (CECs) of up to several equivalents per kilogram (Haggerty and Bowman 1994).

Because of the exchangeable cations, zeolites are polar adsorbents. Molecules such as water or ammonia (high dipole), CO_2, N_2 (quadrupolar) or aromatic hydrocarbons (π layer interaction) therefore adsorb more strongly than nonpolar compounds of similar molecular weight. This affinity generally increases with increasing charge on the exchangeable cation and decreasing cation radius, but its effect may be masked by water, which, because it is strongly bound to a zeolite, will reduce the zeolite's affinity for other, less polar molecules. Aqueous sorption has considerable amounts of water present in the intracrystalline fluid (Ruthven 1988).

Although most zeolites are strongly hydrophilic (because the strongly polar water molecule interacts with the cation), the zeolites with a high silica content (nonpolar surfaces) are actually hydrophobic because water is adsorbed less strongly than most organics. The adsorption is limited to van der Waals forces, and water is adsorbed less strongly than the more polarizable organics (Ruthven 1988). The hydrophilic zeolites may not separate volatile organic compounds (VOCs) well in a humid atmosphere, where complete drying may not occur between sorption events (Blocki 1993).

Liquid and concentration-dependent surface diffusion both contribute to macropore diffusion (Robinson*, et al.* 1994). Diffusivities (at 600 K) range from 10^{-6} - 10^{-7} cm^2/s for benzene and p-xylene to 10^{-14} - 10^{-15} cm^2/s for hexamethylbenzene and anthracene. Although diffusivity changes cannot be correlated directly to molecular weight, molecular length, or critical molecular diameter sequence, the diffusivities generally tend to decrease with increasing sorbate size. Diffusivity instead correlates well with the sorbate's moment of inertia, suggesting that restrictions of the rotational freedom of the sorbate molecule affects diffusivity. This pattern indicates that the diffusion of sterically hindered planar molecules within the pores of a zeolite is controlled primarily by entropy effects, not because the pore size is too small. Therefore, a

sharp cutoff of sorbate size exists and, for molecules larger than the cutoff and whose deformation is sterically hindered, essentially no intracrystalline pore penetration and sorption exist (Ruthven and Kaul 1993b).

Organic Removal Capability

Hydrophobic zeolites generally are non-flammable, temperature-resistant (up to 1000°C), inert to many polar and nonpolar solvents, and are efficient adsorbents for a wide concentration range (Blocki 1993). The saturation capacity is expected to be one molecule per pore, and the adsorption isotherms for many higher weight aromatic hydrocarbons, such as benzene, toluene, xylene, mesitylene, tetramethylbenzene, naphthalene, hexamethylbenzene, dimethylnaphthalene, and anthracene, approach this saturation capacity. There is very little difference between either the isotherms or heats of sorption for different aromatic sorbates with the same carbon number. Therefore, for sufficiently large molecules, steric restrictions of the pores reduce the contact between neighboring molecules and, therefore, their potential for interaction that would prevent sorption (Ruthven and Kaul 1993a).

The higher molecular weight aromatics are very strongly adsorbed, and intracrystalline diffusion is quite slow and temperature dependent. The sorption capacity, however, is essentially independent of temperature, reflecting the tendency of the larger molecules to average out the effect of adsorbent heterogeneities (Ruthven and Kaul 1993a). Zeolites can also sorb unsaturated hydrocarbons with the sorption 'strength' pattern as follows: aromatics > olefins > paraffins (Ruthven 1988). However, unlike activated carbon with its variety of pore sizes, hydrophobic zeolite is slower at separating some relatively common solvents such as xylene because the solvent molecules' diameters are less than the hydrophobic zeolite's pore sizes (Blocki 1993).

Modifying the surface of a zeolite by initially performing ion-exchange with a cationic surfactant can increase the sorption capacity for organics that do not sorb well to natural zeolite. Quarternary amine (HDTMA)-modified zeolites can remove chlorinated aliphatic compounds and benzene derivatives from aqueous solution by a partitioning-like mechanism without lowering the zeolite's naturally high-sorption affinity for transition metal cations such as lead (Eyde 1993; Haggerty and Bowman 1994).

Inorganic Removal Capability

Because of its net negative charge, natural zeolite does not sorb anions well, if at all (Eyde 1993). Surface modification, such as ion-exchange with cationic surfactants, has improved the ability of zeolite to sorb anions and other compounds that natural zeolite did not sorb well. These sorbed cationic surfactants alter the surface charge of the zeolite, thus allowing it to sorb anions and other compounds of interest. Removal of inorganic oxyanions, such as chromate, selenate and sulfate from aqueous solutions improved from nearly zero sorption when a clinoptilolite-dominated zeolite was modified by 140 mmol/kg zeolite (15 meq/g) of hexadecyltrimethylammonium (HDTMA). Anion sorption was greatest when the HDTMA satisfied the zeolite's total external cation-exchange capacity. Anion retention (4 mmol/kg for CrO_4 and >2 mmol/kg for SeO_4 compared to 1 mmol/kg for both on natural, unmodified zeolite) resulted from the formation of an HDTMA-anion precipitate on the zeolite surface (Eyde 1993; Haggerty and Bowman 1994).

Some zeolites are unstable at low pH because the aluminum in the framework is hydrolyzed, and so one approach to exchanging transition metals at low pH is to first form ammonia complexes by dissolving them in dilute aqueous ammonium hydroxide and then carrying out the exchange at high pH (Vaughn 1988). The HDTMA-modified surface, however, is stable at low pH, higher ionic strength and with organic solvents (Eyde 1993; Haggerty and Bowman 1994). For the US Bureau of Mines, zeolites are an alternative to conventional precipitation removal techniques for metals such as lead (Eyde 1993).

Enretech

ENRETECH I is a light-weight, non-toxic, 100% cellulose product (waste from cotton milling) that can be used to clean up oil spills, especially in areas where it is difficult for people to transport themselves and their supplies to the spill and clean it up. It can also be used in areas such as tank storage sites, fueling locations, oil production fields, and oil field pipe treatment yards to collect slow leaks. ENRETECH I is also effective at cleaning up fuel, oil, paint, or coolant spills on highways (RAM Services, Inc. 1995). The ENRETECH I material has the consistency of blown-in fiberglass or mineral wool insulation.

Forest Products Agrofiber

The Forest Products Research Lab agrofiber product was developed as both an economic oil adsorbent and as an economic ion-exchange medium for pollutant removal from water. Kenaf and jute fibers, along with forest wastes such as barks and pine needles, have been found to efficiently remove copper from water. Chemical treatment of the kenaf with reactive yellow-2 significantly increased the adsorption capacity of the kenaf for copper (Forest Products Research Lab 1995).

Gunderboom and EMCON Filter Fabrics

The Gunderboom filter fabric is a woven textile that is marketed as a sorbent fabric for oil spill cleanups. The EMCON filter fabric is a woven fabric that was sold for use in stormwater treatment devices. Emcon North West in Bothell, WA developed it for use in existing storm sewer inlets. It is currently being marketed as the "Type I Catchbasin Filter" (Foss Environmental Services in Seattle, WA).

Limitations of the Literature Review

For most of the investigated media, very little information is available regarding their ability to remove pollutants from a mixed-component influent and what information is available may not be applicable to stormwater runoff treatment. This is because the work was performed using continuous filtration and/or the influent concentration was many times greater than the pollutant concentrations typically found in urban runoff. Complete information on design life and maintenance requirements is not available. This project was designed to supplement the available information about these filters. In particular, the project was designed in order to determine the life of a filter in the field and to investigate any potential maintenance problems. Testing was done on a laboratory-scale using actual stormwater runoff to address these issues. The following two chapters detail the results of the laboratory-scale tests. Future work will examine selected filter media at a pilot-scale.